Classification of Polymerization Process

In polymer chemistry, **polymerization** is a process of reacting monomer molecules together in a chemical reaction to form polymer chains or three-dimensional networks. There are many forms of polymerization and different systems exist to categorize them.



*** Introduction:**

In chemical compounds, polymerization can occur via a variety of reaction mechanisms that vary in complexity due to the functional groups present in the reactants and their inherent steric effects. In more straightforward polymerizations, alkenes form polymers through relatively simple radical reactions; in contrast, reactions involving substitution at a carbonyl group require more complex synthesis due to the way in which reactants polymerize. Alkanes can also be polymerized, but only with the help of strong acids.

As alkenes can polymerize in somewhat straightforward radical reactions, they form useful compounds such as polyethylene and polyvinyl chloride (PVC), which are produced in high tonnages each year due to their usefulness in manufacturing processes of commercial products, such as piping, insulation and packaging. In general, polymers such as PVC are referred to as "**homopolymers**," as they consist of repeated long chains or structures of the same monomer unit, whereas polymers that consist of more than one monomer unit are referred to as copolymers (or co-polymers).

Other monomer units, such as formaldehyde hydrates or simple aldehydes, are able to polymerize themselves at quite low temperatures (ca. -80 °C) to form trimers; molecules consisting of 3 monomer units, which can cyclize to form ring cyclic structures, or undergo further reactions to form tetramers, or 4 monomer-unit compounds. Such small polymers are referred to as oligomers. Generally, because formaldehyde is an exceptionally reactive electrophile it allows nucleophilic addition of hemiacetal intermediates, which are in general short-lived and relatively unstable "mid-stage" compounds that react with other molecules present to form more stable polymeric compounds.

There are two main classes of polymerization reaction mechanisms: step-growth polymerization and chain-growth polymerization.

Step-growth polymerization:

Step-growth polymerization refers to a type of polymerization mechanism in which bi-functional or multifunctional monomers react to form first dimers, then trimers, longer oligomers and eventually long chain polymers. Many naturally occurring and some synthetic polymers are produced by step-growth polymerization, e.g. polyesters, polyamides, polyurethanes, etc. Due to the nature of the polymerization mechanism, a high extent of reaction is required to achieve high molecular weight. The easiest way to visualize the mechanism of a step-growth polymerization is a group of people reaching out to hold their hands to form a human chain – each person has two hands (= reactive sites). There also is the possibility to have more than two reactive sites on a monomer: In this case branched polymers production takes place.

IUPAC deprecates the term step-growth polymerization and recommends use of the terms polyaddition, when the propagation steps are addition reactions and no molecules are evolved during these steps, and polycondensation when the propagation steps are condensation reactions and molecules are evolved during these steps.



A generic representation of a step-growth polymerization. (Single white dots represent monomers and black chains represent oligomers and polymers)

Each step of step-growth (or step) polymerization may involve the combination of two polymer molecules of any lengths to form a longer polymer molecule.

The average molar mass increases slowly and long chains are formed only late in the reaction. Most step-growth polymers are also classified as condensation polymers, since a small molecule such as water is lost when the polymer chain is lengthened. For example, polyester chains grow by reaction of alcohol and carboxylic acid groups to form ester links with loss of water. However, there are exceptions; for example polyurethanes are step-growth polymers formed from isocyanate and alcohol bifunctional monomers) without loss of water or other small molecule, and are classified as addition polymers rather than condensation polymers.

Step-growth polymers increase in molecular weight at a very slow rate at lower conversions and reach moderately high molecular weights only at very high conversion (i.e., >95%).

<u>Polyamide:</u>

One important class of step-growth polymerization (condensation polymer) is the formation of polyamides. They arise from the reaction of carboxylic acid and an amine. Examples include nylons and proteins. When prepared from amino-carboxylic acids, e.g. amino acids, the stoichiometry of the polymerization includes co-formation of water

$$n H_2N-X-CO_2H \rightarrow [-HN-X-C(O)-]_n + n H_2O$$

When prepared from diamines and dicarboxylic acids, e.g. the production of nylon 66, the polymerization produces two molecules of water per repeat unit

$$n H_2N-X-NH_2 + n HO_2C-Y-CO_2H \rightarrow [-HN-X-NHC(O)-Y-C(O)-]_n + 2n H_2O$$

$$n \xrightarrow{O}_{HO} O + n H_2 N - R' - N H_2 \longrightarrow \begin{bmatrix} O & O \\ H & C - R - C' + n H_2 N - R' - N H_2 \\ H & H \end{bmatrix}_n + 2 H_2 O$$

General chemical structure of one type of condensation polymer

Polyester:

Another important class of step-growth polymerization is the formation of polyamides polyesters. They arise from the reaction of carboxylic acid and an alcohol. Examples include polyesters, e.g. polyethyleneterephthalate

$$n \text{ HO-X-OH} + n \text{ HO}_2\text{C-Y-CO}_2\text{H} \rightarrow [\text{-O-X-O}_2\text{C-Y-C(O)-}]_n + (3n-2) \text{ H}_2\text{O}$$

• Typical step-growth polymerization reactions: Reaction Polymer n HO-(CH2), COTH -> HO F(CH2), CO-O], H + (n-1)H20 Polyester n H2N-R-COOH - HENH-R-COIn + (n-1) H20 Polyamide $nH_2N-R-NH_2 + nH00C-R'-(00H) \rightarrow H - (NH-R-NH-CO-R'-CO - nOH + (2n-1)H_2O$ n HO-R-OH + NOCN-R'-NCO → EOR-O-E-NH-R'NH-EIn Polyurettanes n HOOC - R- COOH → HO - CO - R - "- O - H + (m-1) H20 Polyanhydride Polysiloxane n 1+0 - Si-CH3 Phenol-formal no + nctzo -0 +(n-1) H20 formation : The assumption so far have been that all bifunctional monomers in step-growth reaction form linear polymers. This is not always true and competitive side such as cyclization may occur, as with certain reactions hydromyacids which may form lactones or lactams if an amino acid is used. HO-R-COOTI -> R + HO To gauge the importance of such reactions consideration must be given to the Thermodynamic and Kinetic aspects of ring formation. A study of sing strain in cycloalkames has shown that 3- and 1- membered rings are severely strained but that decreases dramatically for 5, 6, or 7-membered rings, Then increases again up to 11 before decreasing for very large rings. In

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addition to the thermodynamic stability, the kinetic feasibility of two suitable functional groups being in juxtaposition to react must also be considered. This probability decreases with increasing ring size and again 5,6, or 7-membered rings are are favoured and will form in preference to a linear chain when possible.

• Non-linear step-growth reaction:

A monomen with functionality of 3 or more will introduce branching in a polymer and will ultimately form a crosslinked macrostructure or network even at dow fractional conversion. The point at which a tree-like tropology transits to a network is known as the fel point because it is signalled by an abrupt change in viscosity. One of-Ite earliest so-called thermosets is known as backlife. It is not always water that is released in step - growth polymerisation: in acyclic diene metalthesis or ADMET dienes polymerize with loss of eithere.

* Chain-growth polymerization:

In chain-growth (or chain) polymerization, the only chain-extension reaction step is the addition of a monomer to a growing chain with an active center such as a free radical or ion. Once the growth of a chain is initiated by formation of an active center, chain propagation is usually rapid by addition of a sequence of monomers.

Chain-growth polymerization (or addition polymerization) involves the linking together of molecules incorporating double or triple carbon-carbon bonds. These unsaturated *monomers* (the identical molecules that make up the polymers) have extra internal bonds that are able to break and link up with other monomers to form a repeating chain, whose backbone typically contains only carbon atoms. Chain-growth polymerization is involved in the manufacture of polymers such as polyethylene, polypropylene, and polyvinyl chloride (PVC).

<u>Steps of chain growth polymerization:</u>

Typically, chain polymerization must contain chain initiation and chain propagation. Chain transfer and chain termination do not always happen in a chain-growth polymerization.

1. <u>Chain initiation</u>: Chain initiation is the process of initially generating a chain carrier (chain carriers are some intermediates such as radical and ions in chain propagation process) in a chain polymerization. According to different ways of energy dissipation, it can be divided into thermal initiation, high energy initiation, and chemical initiation, etc.

2. <u>Chain propagation:</u> IUPAC defined chain propagation as an active center on the growing polymer molecule, which adds one monomer molecule to form a new polymer molecule which is one repeat unit longer with a new active center.

3. <u>Chain transfer</u>: The polymerization process does not have to undergo chain transfer. Chain transfer means that in a chain polymerization, the active center of the polymer A takes an atom from B molecule and terminates. The B molecule produces a new active center instead. It can happen in free radical polymerization, ionic polymerization and coordination polymerization. Generally, chain transfer will generate by-product.

4. <u>Chain termination</u>: Chain termination refers to in chain polymerization process, active center disappears, resulting in the termination of chain propagation. It is different from chain transfer. During the chain transfer process, the active point only shifts to another molecule but does not disappear.

<u>Classes of chain growth polymerization</u>

<u>Radical polymerization</u>:

Based on definition from IUPAC, radical polymerization is a chain polymerization in which the kinetic-chain carriers are radicals. Usually, the growing chain end bears an unpaired electron. Free radicals can be initiated by many methods such as heating, redox reactions, ultraviolet radiation, high energy irradiation, electrolysis, sonication, and plasma. Free radical polymerization is very important in polymer chemistry. It is one of the most developed methods in chain-growth polymerization. Currently, most polymers in our daily life are synthesized by free radical polymerization, such as polyethylene, polystyrene, polyvinyl chloride, polymethyl methacrylate, polyacrylonitrile, polyvinyl acetate, styrene butadiene rubber, nitrile rubber, neoprene, etc.

withing reprint it D9 nitiators: Initiation of a free-radical polymerization requires the produ-ction of free radicals in the presence of the unsalurated monomer. The initiating free radicals can be produced directly from the monomes (by irradiation with high energy radiation for example), but it is more normal for the radicals to be generated from the added initiator, Such an initiator is usually a molecule that can be decomposed thermally or by irradiation to yield a pair of initiating radicals Typical radical producing reactions are: 1) Thermal decomposition: Thermal decomposition can be usually applied to organic peroxides (dialky) peroxides, diacy-Iperoaides, hydroperoxides) on azo compounds. a) $\bigcirc \overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset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 $d(H_3c)e^{-N=N-e(cH_3)_2} \longrightarrow 2(cH_3)_2^{cN} + N_2$ 2] Photolysis: Photolysis is applicable to metal iodides, metal alkyls, and azo compounds e.g. x, x'- azobisisobutyronitrile (AIBN) is decomposed by radiation with a wavelength of 360 nm. (SH3) 3] Redox reactions: The reaction between the ferrous ion and hydrogen peroxide in solution produces hydroxyl radicals, $H_20_2 + Fe^{2+} \rightarrow Fe^{3+} + H_0^0 + \delta H_1$ Alkyl hydroperoxides may be used in place of H2O2. A similar reaction is observed when cerium(IV) sulphate oridizes an alcohol; an alcohol; $R - CH_2OH + Ce^{4+} \rightarrow Ce^{3+} + H^+ + R - CH - OH$ 4) Ionizing radiation: x, B, 8- or x-rays may be used to initiate a polymerization, by causing the ejection of an electron followed by dissociation and electron capture to produce à radical Ejection: C ~~ + e Dissociation: c+ ~ A + a e capture : g' + e -> à 5) Persulphates are useful in emulsion polymerizations where decomposition occurs in the aqueous phase and the radical diffuses into a hydrophobic, monomer containing droplet. $S_2 O_8^{2-} - 2 S O_4^{-}$ Monomers for free radical polymerization: A wide variety of unsaturated organic compounds can be induced to undergo free radical polymerization. Some of these are listed in the following table. In general, the monomer structure can be represented by The formula cH2 = CHR where the group R is an organic unit? a halogen. on pseudo-halogen ligand, or even an inorganic residue,

CH2 = CH-Ph styreme · Vinylidene chloride. CHz=ccl2. a-Methylstyrene ct2 = c(Me)-ph Teirafluoro ettylene cf2 = cf2 1,3-Butadiene CH2=CH-CH=CH2 Acrylonitoile CH2=CH-CN nelty methacrylate CH_=C(Me)-COOME Vinyl ester N-Vinyl by molidone ch2=CH-0-COR NTO Eltylene $CH_2 = CH_2$ H,C=EH Vinyl chloride CH2 = CH-CL Acrylamide ·CH2=CH-CONH2 Table: Monomers for free-radical polymerization • Reaction of initiator radicals with monomer: The second important-step in a radical polymerization is the addition of the initiating radical to a monomer molecule. Only a fraction of the initiating radicals formed behave in this way, because it is generally found that the rate of chain initiation is lower than The rate at which the initiating radicals are formed. This wastage of initiating radicals occurs because of several possible fast reactions which competer with the original reaction i.e, reaction with monomer. These alternative reactions are given the below____ + Radical combination within the solvent cage: R+R - R-R → Secondary recombination outside the cage: R+R → R-R → Reaction with polymer radicals: R + · · · · · · · · R - ···· * Reaction with initiator: R+R-R - R+R + Radical abstraction : R+H-R -+ R-H + R A Reaction with relivent: R + dgc - R-d + dze > Chain initiation: R+ monomer -> R-monomer Possible fates of initiator radicals Suantitative studies indicate that the efficiency of initiation lies most often between 0.1 and 0.8. It correlates approximately with the viscosity of the medium and is approximately independent of temperature. ron

• Radical chain propagation: Chain propagation involves the addition of a free radical to the double bond of a monomer molecule. The product must itself be a free radical and the process can be repeated. In fact, it is common for thousands of momener molecules to add successively to the end of the chain. The most likely form of monomer addition is called head-to-tail addition. Reaction(1) illustrates this behaviowz. Alternatively, the addition may involve a head to head (reaction 2) on tail to tail reaction (3). Although it might be supposed that species (I), (II) and (II) might be distributed randomly through the molecular chain, it is, in fact, found That thead to - tail linkages (I) are in great excess. For example, in poly(viny) alcohol), -EctyCH(OH) -, it has been found that the percentage of (II) and (III) is only 1.1% in polymer prepared at 25°C and only 1.8% at 100°C. $R - M - cH_2 - c' + c' = cH_2 \rightarrow R - M - eH_2 - c' - c' - cH_2 - (2)$ (B) × × (B) × × (B) × × (B) × × (CH_2 - c') (\mathbf{B}) $R - M - c_{12} - c_{12} + c_{12} = c_{1} \longrightarrow R - M - c_{12} - c_{12} - c_{12} - c_{12} - c_{13}$ × (c) XIIIX The principal reason for the preference of head-to-tail addition lies in the greater thermodynamic stability of a free radical such as (A) relative to that of one such as (c), and perhaps also to steric inhibition of-step such as o (2). It can, in fact, be shown that the addition of methyl radicals to propylene, ct2 = cH-Me is more favourable if the methyl and radical adds to the och_= ' unit rather Than to the = CH(Me)? component,

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Dehain transfer reaction: In an ideal free radicat polymerization chain become initialed, they propagate linearly and then they are terminated. Such ideal circumtances are often found in ionic polymerizations, but only narely in free radical processes. The deviation from ideality occurs when a propagating oligomen on polymer radical reacts with another molecule, not by addition but by abstraction. By "abstraction" we mean a process in which a radical fragment is removed from the second molecule with concurrent generation of a radical redical residue from that record molecule (reaction 4). Second molecule could be monomer, solvent, initiation, polymer molecule, or other molecules deliberately or accidentally incorporated into the reaction mixime. $R - M - cH_2 - \frac{1}{e} + YZ \longrightarrow R - M - cH_2 - \frac{1}{e} + \frac{1}{Z} - (4)$ It is important to note that although the polymer chain (IV) is now effectively terminated, z may initiate a new. chain if its reactivity is comparable to that of a normal propagating mole radical. Such a process is called chain Transfer. when the second molecule is a polymer molecule, the ultimate result is generally the formation of a branched polymer. Thus if hydrogen radical abstraction from a polymer leads to The formation of a residue such as (\mathbf{V}) , the radical site on this residue can initiate growth of a branch, H-e-x such as (VI). R-M-cy-c-M-R' R-M-cy-c-M (VI) 95- The second molecule YZ yields a radical fragment, i which is unreactive toward the monomer, the subtance yz is termed as

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> <u>Ionic polymerization</u>:

Based on IUPAC, ionic polymerization is a chain polymerization in which the kinetic-chain carriers are ions or ion pairs. It can be further divided into **a] cationic polymerization** and **b] anionic polymerization**. Ionic polymerization is widely used in our daily life. A lot of common polymers are generated by ionic polymerization such as butyl rubber, polyisobutylene, polyphenylene, polyoxymethylene, polysiloxane, polyethylene oxide, high density polyethylene, isotactic polypropylene, butadiene rubber, etc. Living anionic polymerization was developed since the 1950s, the chain will remain active indefinitely unless the reaction is transferred or terminated deliberately, which realizes the control of molar weight and PDI.

a] <u>Cationic</u> polymerization:

Cationic polymerization is a type of chain growth polymerization in which a cationic initiator transfers charge to a monomer which then becomes reactive. This reactive monomer goes on to react similarly with other monomers to form a polymer. The types of monomers necessary for cationic polymerization are limited to alkenes with electron-donating substituents and heterocycles. Similar to anionic polymerization reactions, cationic polymerization reactions are very sensitive to the type of solvent used. Specifically, the ability of a solvent to form free ions will dictate the reactivity of the propagating cationic chain. Cationic polymerization is used in the production of polyisobutylene (used in inner tubes) and poly(N-vinylcarbazole) (PVK)

Monomers:

Monomer scope for cationic polymerization is limited to two main types:

1. alkene and 2. heterocyclic monomers. Cationic polymerization of both types of monomers occurs only if the overall reaction is thermally favorable. In the case of alkenes, this is due to isomerization of the monomer double bond; for heterocycles, this is due to release of monomer ring strain and, in some cases, isomerization of repeating units. Monomers for cationic polymerization are nucleophilic and form a stable cation upon polymerization.

1. Alkenes:

Cationic polymerization of olefin monomers occurs with olefins that contain electron-donating substituents. These electron-donating groups make the olefin nucleophilic enough to attack electrophilic initiators or growing polymer chains. At the same time, these electron-donating groups attached to the monomer must be able to stabilize the resulting cationic charge for further polymerization. Some reactive olefin monomers are shown below in order of decreasing reactivity, with heteroatom groups being more reactive than alkyl or aryl groups. Note, however, that the reactivity of the carbenium ion formed is the opposite of the monomer reactivity.



Decreasing reactivity of alkene monomers

2. Heterocyclic monomers:

Heterocyclic monomers that are cationically polymerized are lactones, lactams and cyclic amines. Upon addition of an initiator, cyclic monomers go on to form linear polymers. The reactivity of heterocyclic monomers depends on their ring strain. Monomers with large ring strain, such as oxirane, are more reactive than 1,3-dioxepane which has considerably less ring strain. Rings that are six-membered and larger are less likely to polymerize due to lower ring strain.



Examples of heterocyclic monomers

Synthesis:

A] Initiation:

Initiation is the first step in cationic polymerization. During initiation, a carbenium ion is generated from which the polymer chain is made. The counterion should be non-nucleophilic, otherwise the reaction is terminated instantaneously. There are a variety of initiators available for cationic polymerization, and some of them require a coinitiator to generate the needed cationic species.

Strong protic acids can be used to form a cationic initiating species. High concentrations of the acid are needed in order to produce sufficient quantities of the

cationic species. The counterion (A⁻) produced must be weakly nucleophilic so as to prevent early termination due to combination with the protonated alkene. Common acids used are phosphoric, sulfuric, fluoro-, and triflic acids. Only low molecular weight polymers are formed with these initiators.



Initiation by protic acids

Lewis acids are the most common compounds used for initiation of cationic polymerization. The more popular Lewis acids are SnCl₄, AlCl₃, BF₃, and TiCl₄. Although these Lewis acids alone are able to induce polymerization, the reaction occurs much faster with a suitable cation source. The cation source can be water, alcohols, or even a carbocation donor such as an ester or an anhydride. In these systems the Lewis acid is referred to as a coinitiator while the cation source is the initiator. Upon reaction of the initiator with the coinitiator, an intermediate complex is formed which then goes on to react with the monomer unit. The counterion produced by the initiator-coinitiator complex is less nucleophilic than that of the Brønsted acid A⁻ counterion. Halogens, such as chlorine and bromine, can also initiate cationic polymerization upon addition of the more active Lewis acids.



Initiation with boron trifluoride (coinitiator) and water (initiator)

Stable carbenium ions are used to initiate chain growth of only the most reactive alkenes and are known to give well defined structures. These initiators are most often used in kinetic studies due to the ease of measuring the disappearance of the carbenium ion absorbance. Common carbenium ions are trityl and tropylium cations.



Initiation with trityl carbenium ion

Ionizing radiation can form a radical-cation pair that can then react with a monomer to start cationic polymerization. Control of the radical-cation pairs are difficult and often depend on the monomer and reaction conditions. Formation of radical and anionic species is often observed.



Initiation using ionizing radiation

B] Propagation

Propagation proceeds by addition of monomer to the active species, i.e. the carbenium ion. The monomer is added to the growing chain in a head-to-tail fashion; in the process, the cationic end group is regenerated to allow for the next round of monomer addition.



General propagation pathway

Effect of temperature

The temperature of the reaction has an effect on the rate of propagation. The overall activation energy for the polymerization (E) is based upon the activation energies for the initiation (E_i), propagation (E_p), and termination (E_t) steps:

$$E = E_i + E_p - E_t$$

Generally, E_t is larger than the sum of E_i and E_p , meaning the overall activation energy is negative. When this is the case, a decrease in temperature leads to an increase in the rate of propagation. The converse is true when the overall activation energy is positive.

Chain length is also affected by temperature. Low reaction temperatures, in the range of 170–190 K, are preferred for producing longer chains. This comes as a result of the activation energy for termination and other side reactions being larger than the activation energy for propagation. As the temperature is raised, the energy barrier for the termination reaction is overcome, causing shorter chains to be produced during the polymerization process.

Effect of solvent and counterion

The solvent and the counterion (the gegen ion) have a significant effect on the rate of propagation. The counterion and the carbenium ion can have different associations according to intimate ion pair theory; ranging from a covalent bond, tight ion pair (unseparated), solvent-separated ion pair (partially separated), and free ions (completely dissociated).

 ~~~RX	~~~R+X-	~~~R+/X-	~~~R+ + X-
covalent	tight ion pair	solvent-separated ion pair	free ions

Range of associations between the carbenium ion  $(R^+)$  and gegen ion  $(X^-)$ 

The association is strongest as a covalent bond and weakest when the pair exists as free ions. In cationic polymerization, the ions tend to be in equilibrium between an ion pair (either tight or solvent-separated) and free ions. The more polar the solvent used in the reaction, the better the solvation and separation of the ions. Since free ions are more reactive than ion pairs, the rate of propagation is faster in more polar solvents.

The size of the counterion is also a factor. A smaller counterion, with a higher charge density, will have stronger electrostatic interactions with the carbenium ion than will a larger counterion which has a lower charge density. Further, a smaller counterion is more easily solvated by a polar solvent than a counterion with low charge density. The result is increased propagation rate with increased solvating capability of the solvent.

## **C]** Termination

Termination generally occurs by unimolecular rearrangement with the counterion. In this process, an anionic fragment of the counterion combines with the propagating chain end. This not only inactivates the growing chain, but it also terminates the kinetic chain by reducing the concentration of the initiator-coinitiator complex.



Termination by combination with an anionic fragment from the counterion

#### **D]** Chain transfer

Chain transfer can take place in two ways. One method of chain transfer is hydrogen abstraction from the active chain end to the counterion. In this process, the growing chain is terminated, but the initiator-coinitiator complex is regenerated to initiate more chains.



Chain transfer by hydrogen abstraction to the counterion

The second method involves hydrogen abstraction from the active chain end to the monomer. This terminates the growing chain and also forms a new active carbenium ion-counterion complex which can continue to propagate, thus keeping the kinetic chain intact.



Chain transfer by hydrogen abstraction to the monomer

#### Cationic ring-opening polymerization

Cationic ring-opening polymerization follows the same mechanistic steps of initiation, propagation, and termination. However, in this polymerization reaction, the monomer units are cyclic in comparison to the resulting polymer chains which are linear. The linear polymers produced can have low ceiling temperatures, hence end-capping of the polymer chains is often necessary to prevent depolymerization.^[6]



*Cationic ring-opening polymerization of oxetane involving (a and b) initiation, (c) propagation, and (d) termination with methanol* 

#### b] <u>Anionic</u> <u>polymerization</u>:

Anionic addition polymerization is a form of chain-growth polymerization or addition polymerization in which the growing chain bears a negative charge. Often anionic polymerization involves living polymerizations, which allows control of structure and composition.

#### Initiators:

Initiators are selected based on the reactivity of the monomers. Highly electrophilic monomers such as cyanoacrylates require only weakly nucleophilic initiators, such as amines, phosphines, or even halides. Less reactive monomers such as styrene require powerful nucleophiles such as butyl lithium. Reaction of intermediate strength is used for monomers of intermediate reactivity such as vinylpyridine.

The solvent used in anionic addition polymerizations are determined by the reactivity of both the initiator and nature of the propagating chain end. Anionic species with low reactivity, such as heterocyclic monomers, can use a wide range of solvents.^[4]

#### Initiation by electron transfer

Initiation of styrene polymerization with sodium naphthalene proceeds by electron transfer from the naphthalene radical anion to the monomer. The resulting radical dimerizes to give a dilithio compound, which then functions as the initiator. Polar solvents are necessary for this type of initiation both for stability of the anionradical and to solvate the cation species formed. The anion-radical can then transfer an electron to the monomer. Initiation can also involve the transfer of an electron from the alkali metal to the monomer to form an anion-radical. Initiation occurs on the surface of the metal, with the reversible transfer of an electron to the adsorbed monomer.

#### **Initiation** by strong anions

Nucleophilic initiators include covalent or ionic metal amides, alkoxides, hydroxides, cyanides, phosphines, amines and organometallic compounds (alkyllithium compounds and Grignard reagents). The initiation process involves the addition of a neutral or negative nucleophile to the monomer. The most commercially useful of these initiators has been the alkyllithium initiators. They are primarily used for the polymerization of styrenes and dienes.

Monomers activated by strong electronegative groups may be initiated even by weak anionic or neutral nucleophiles (i.e. amines, phosphines). Most prominent example is the curing of cyanoacrylate, which constitutes the basis for superglue. Here, only traces of basic impurities are sufficient to induce an anionic addition polymerization or zwitterionic addition polymerization, respectively.

#### Monomers for anionic polymerization:

Typical monomers that can be polymerized by anionic mechanism include styrene, butadiene, isoprene, methyl methacrylate, acrylonitrile cyanoacrylate, acrolein, vinylpyridine, vinyl sulfone, vinyl sulfoxide, and vinyl silanes. The important thing is that monomers which are suitable for anionic polymerization generally contain electron withdrawing substituent groups.



Cyclic monomer



Many cyclic compounds are susceptible to ring-opening polymerization. Epoxides, cyclic trisiloxanes, some lactones, lactides, amino acid N-carboxyanhydrides, and cyclic carbonates

In order for polymerization to occur with vinyl monomers, the substituents on the double bond must be able to stabilize a negative charge. Stabilization occurs through delocalization of the negative charge. Because of the nature of the carbanion propagating center, substituents that react with bases or nucleophiles either must not be present or be protected.

#### **Propagation:**

Propagation involves the successive insertion of monomer molecules into the terminal ionic bond. This process of chain growth continues until all the monomers have been consumed or until the reaction is terminated.



#### Chain transfer:

Chain transfer or chain branching does not occur to any appreciable extent with anionic systems, and this is especially true if the reaction is carried out at low temperatures.

#### Termination:

Termination of the chains occurs accidentally or deliberately when the active chain end reacts with a molecule of carbon dioxide or with water, alcohols, or other protonic reagents. However, it is important to note that if termination reagents are absent, the chains could remain active indefinitely. In practice, it is impossible to remove all traces of water molecules from the inside of glass equipments and, even if that were possible, the Si-OH groups at the glass surface could presumably function as termination agents.



#### > <u>Coordination</u> <u>polymerization</u>:

Based on definition from IUPAC, coordination polymerization is a chain polymerization that involves the preliminary coordination of a monomer molecule with a chain carrier. The monomer is firstly coordinated with the transition metal active center, and then the activated monomer is inserted into the transition metal-carbon bond for chain growth. In some cases, coordination polymerization is also called insertion polymerization or complexing polymerization. Advanced coordination polymerizations can control the tacticity, molecular weight and PDI of the polymer effectively. In addition, the racemic mixture of the chiral metallocene can be separated into its enantiomers. The oligomerization reaction produces an optically active branched olefin using an optically active catalyst.

## Living polymerization:

Living polymerization was first introduced by Michael Szwarc in 1956. Based on definition from IUPAC, it is a chain polymerization from which chain transfer and chain termination are absent. As there is no chain-transfer and chain termination, the monomer in the system is consumed and the polymerization is stopped when the polymer chain remains active. Once the new monomer is added, the polymerization can proceed. Due to the low PDI and predictable molecular weight, living polymerization is at the forefront of polymer research. It could be further divided into living free radical polymerization, living ionic polymerization and living ring-opening metathesis polymerization, etc.

Living anionic polymerization was demonstrated by Szwarc and co workers in 1956. Their initial work was based on the polymerization of styrene and dienes. One of the remarkable features of living anionic polymerization is that the mechanism involves no formal termination step. In the absence of impurities, the carbanion would still be active and capable of adding another monomer. The chains will remain active indefinitely unless there is inadvertent or deliberate termination or chain transfer. This gave rise to two important consequences:

**1.** The number average molecular weight,  $M_n$ , of the polymer resulting from such a system could be calculated by the amount of consumed monomer and the initiator used for the polymerization, as the degree of polymerization would be the ratio of the moles of the monomer consumed to the moles of the initiator added.

 $\mathbf{M}_{\mathbf{n}} = \mathbf{M}_{\mathbf{0}} \begin{bmatrix} \mathbf{M} \end{bmatrix}_{\mathbf{0}}$ , where  $\mathbf{M}_{\mathbf{0}} =$  formula weight of the repeating unit,  $[\mathbf{M}]_{\mathbf{0}} =$  initial concentration of the monomer, and  $[\mathbf{I}] =$  concentration of the initiator.

2. All the chains are initiated at roughly the same time. The final result is that the polymer synthesis can be done in a much more controlled manner in terms of the molecular weight and molecular weight distribution (Poisson distribution).

The following experimental criteria have been proposed as a tool for identifying a system as living polymerization system.

- Polymerization until the monomer is completely consumed and until further monomer is added.
- Constant number of active centers or propagating species.
- Poisson distribution of molecular weight
- Chain end functionalization can be carried out quantitatively.

However, in practice, even in the absence of terminating agents, the concentration of the living anions will reduce with time due to a decay mechanism termed as spontaneous termination.

Living cationic polymerization is a living polymerization technique involving cationic propagating species. It enables the synthesis of very well defined polymers (low molar mass distribution) and of polymers with unusual architecture such as star polymers and block copolymers and living cationic polymerization is therefore as such of commercial and academic interest.

In carbocationic polymerization the active site is a carbocation with a counterion in close proximity. The basic reaction steps are:

 $A^+B^- + H_2C=CHR \rightarrow A-CH_2-RHC^+----B^-$ 

## Chain propagation:

 $A-CH_2-RHC^+----B^- + H_2C=CHR \rightarrow A-(CH_2-RHC)_n-CH_2-RHC^+----B^-$ 

## Chain termination:

 $A-(CH_2-RHC)_n-CH_2-RHC^+---B^- \rightarrow A-(CH_2-RHC)_n-CH_2-RHC-B$ 

## Chain transfer:

 $A-(CH_2-RHC)_n-CH_2-RHC^+---B^- \rightarrow A-(CH_2-RHC)_n-CH_2=CR H^+B^-$ 

Living cationic polymerization is characterised by defined and controlled initiation and propagation while minimizing side-reactions termination and chain transfer. Transfer and termination do occur but in ideal living systems the active ionic propagating species are in chemical equilibrium with the dormant covalent species with an exchange rate much faster than the propagation rate. Solution methods require rigorous purification of monomer and solvent although conditions are not as strict as in anionic polymerization. Common monomers are vinyl ethers, alpha-methyl vinyl ethers, isobutene, styrene, methylstyrene and N-vinylcarbazole. The monomer is nucleophilic and substituents should be able to stabilize a positive carbocationic charge. For example, para-methoxystyrene is more reactive than styrene itself.

Initiation takes place by an initiation/coinitiation binary system, for example an alcohol and a Lewis acid. The active electrophile is then a proton and the counter ion the remaining alkoxide which is stabilized by the Lewis acid. With organic acetates such as cumyl acetate the initiating species is the carbocation  $R^+$  and the counterion is the acetate anion. In the iodine/HI system the electrophile is again a proton and the carbocation is stabilized by the triiodide ion. Polymerizations with Diethylaluminium chloride rely on trace amounts of water. A proton is then accompanied by the counterion  $Et_2AlClOH^-$ . With tert-butyl chloride  $Et_2AlCl$  abstracts a chlorine atom to form the tert-butyl carbocation as the electrophile. Efficient initiators that resemble the monomer are called cationogens. Termination and chain transfer are minimized when the initiator counterion is both non-nucleophilic and non-basic. More polar solvents promote ion dissociation and hence increase molar mass.

Common additives are electron donors, salts and proton traps . Electron donors (e.g. nucleophiles, Lewis bases) for example dimethylsulfide and dimethylsulfoxide are believed to stabilize the carbocation. The addition of salt for example a tetraalkylammonium salt, prevents dissociation of the ion pair that is the propagating reactive site. Ion dissociation into free ions leads to non-living polymerization. Proton traps scavenge protons originating from protic impurities.

## <u>Ring-opening</u> polymerization:

According to definition from IUPAC ring-opening polymerization is a polymerization in which a cyclic monomer yields a monomeric unit which is acyclic or contains fewer cycles than the monomer. Generally, the ring-opening polymerization is carried out under mild conditions, and the by-product is less than the polycondensation reaction and the high molecular weight polymer is easily obtained. Common ring-opening polymerization products include polypropylene oxide, polytetrahydrofuran, polyepichlorohydrin, polyoxymethylene, polycaprolactam and polysiloxane.

## Reversible-deactivation polymerization:

IUPAC stipulates that reversible-deactivation polymerization is a kind of chain polymerization, which is propagated by chain carriers that are deactivated reversibly, bringing them into active-dormant equilibria of which there might be more than one. An example of a reversible-deactivation polymerization is group-transfer polymerization.

Step-growth polymerization	Chain-growth polymerization	
Growth throughout matrix	Growth by addition of monomer only at one end or both ends of chain	
Rapid loss of monomer early in the reaction	Some monomer remains even at long reaction times	
Similar steps repeated throughout reaction process	Different steps operate at different stages of mechanism (i.e. initiation, propagation, termination, and chain transfer)	
Average molecular weight increases slowly at low conversion and high extents of reaction are required to obtain high chain length	Molar mass of backbone chain increases rapidly at early stage and remains approximately the same throughout the polymerization	
Ends remain active (no termination)	Chains not active after termination	
No initiator necessary	Initiator required	

#### * Difference between the Step-growth and Chain-growth polymerization